The Early Days of Chemical Ionization: A Reminiscence

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A narrative account is given of the events leading to the discovery of chemical ionization in the laboratories of the Humble Oil and Refining Company in 1965. The discovery was unplanned in the sense that it resulted from the observation of unanticipated phenomena made in the course of experiments undertaken for a different purpose. However, the sequence of events which occurred is an illustration of the discovery of a practical, useful result from a program of research which was primarily of a basic nature but with ancillary awareness of possible practical implications. *(J Am Soc Mass Spectrom 1990, 1, 277–283)*

This is a retrospective article suggested by Editor Mike Gross in which I shall attempt to give an account of the discovery of chemical ionization mass spectrometry (CIMS). I initially had some concern about the existence of a retrospective tendency in ASMS, for a preoccupation with history is oftentimes an indication that an institution or organization or discipline has matured and perhaps is even entering a decline. However, three milliseconds of reflection brought me to the realization that in the past year or two mass spectrometry has seen the development of methods which produce mass spectra of proteins in the 100,000–300,000 u range (matrix assisted laser desorption and electrospray ionization), and this on top of the ten to fifteen years of marvels associated with massive particle bombardment desorption mass spectrometry. Advances in other subdivisions of the discipline might also be cited. It is obvious that any discipline with that degree of vitality can look back to its history with relative impunity. I digress to say that I have been associated with mass spectrometry now for over forty years, and in that time its history has been one of progress from one exciting peak of interest and discovery to the next. In my opinion the present period is at least as exciting as any that has existed until now.

Mass spectrometry started in the early part of the twentieth century, but even by the end of World War II it was being pursued in only a small number of laboratories. This was especially true of the organic mass spectrometry to which I shall restrict my subsequent remarks. While mass spectrometers were available commercially at the end of the war, they were prohibitively expensive, for a Consolidated Engineering Corp. Model 101 instrument cost about $35,000. Federal funding for scientific research was five to ten years in the future, and to provide a scale of reference, my annual research grant as an instructor and assistant professor at the University of Texas was $200. One could in principle construct an instrument for less than $35,000, but the techniques involved were arcane and not widely known. Petroleum and chemical companies were the only organizations which had both the money and the need for mass spectrometry, and consequently the discipline was dominated by industrial mass spectrometrists, and the contribution that they made to the field was very great. One should also mention the important compilation of mass spectra started by the National Bureau of Standards in about 1947.

The industrial contributions were usually empirical and practical, directed primarily to the development and use of analytical procedures, but fortunately some of the major companies were both affluent enough and enlightened enough to support some basic research. The Humble Oil and Refining Co. (part of what is now Exxon Corporation) in Baytown, Texas, was one of these companies, and in 1951 a small basic research program in mass spectrometry was started under the very able direction of Joe Franklin. I joined the research program shortly after its inception. The rationale for the work was that organic ions, particularly carbocations, are very much involved in a number of very important petroleum refining processes, and Joe Franklin believed that information obtained in the gas phase about the intrinsic properties of these ions would contribute to an understanding of their behavior in practical condensed phase processes.

Our initial research activities involved measuring ionization and appearance potentials using the electron ionization (EI) vanishing current method. While by present standards this method was crude and inaccurate, in fact the measurements (by others as well as by ourselves) were tremendously important, for they gave some of the first quantitative information about the energies of gaseous organic ions. However, we and

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everyone else working in the field of chemical physics mass spectrometry (all 15-25 of us) were tremendously excited by the 1952 paper by the Soviet mass spectrometrist Viktor Talrose and his associate A. K. Lyubimova [1] stating that CH_5^+ existed and was produced by running methane in a mass spectrometer at an elevated pressure (perhaps about 10^{-2} torr). (I might add parenthetically that at this time it was believed by almost all mass spectrometrists that the sky would fall if one tried to operate a mass spectrometer at any pressure higher than about 10^{-6} torr.) Joe Franklin and I resolved to make some high-pressure experiments as soon as prior obligations permitted. We made a few preliminary experiments with our Westinghouse Type LV mass spectrometer (a 90° sector instrument, design resolution about 100), and we found that, indeed, we could raise the pressure in the ion source to about 10 microns (the torr unit of pressure was just beginning to come into use) without catastrophe. Consequently, at our first opportunity to get back to full-time experimental work we started a program of work in the brand new, thrilling field of ion–molecule reactions wherein startling, unexpected reactions occurred without activation energies at rates approaching 10^{-9} $cm^3/(mol \cdot s)$.

Our efforts in making measurements of ion energies were successful enough that Joe Franklin and I were persuaded that we could profitably use a mass spectrometer designed for and dedicated to studies in chemical physics mass spectrometry. We made a proposal to this effect to the company (Humble Oil and Refining Co.), and money was first appropriated for design expenses and then for construction. The amount involved was more than $100,000, which would be somewhere between $500,000 and $1,000,000 in today's dollars. And all of this on the strength of a five-page written proposal and an explanatory conversation with the boss of the laboratory—the good old days!

By the time the design of the new instrument was completed, we had already made a number of studies of ion–molecule reactions using other mass spectrometers in the laboratory, and we had gained enough experience to suspect that providing a high pumping speed on the machine would be desirable. The commercial mass spectrometers of the period were equipped with the most modest of pumping capacities. Mass spectrometers were for the very largest part used only for EI analytical measurements, and consequently the pressures involved were very low (10^{-6}–10^{-5} torr). The gas loads were thus also very low, and the manufacturers were doubtless delighted to save some money by providing only a very limited pumping capacity—only a few tens of liters per second, as best I recall. This was the total pumping on the mass spectrometer tube, and no differential pumping on the analyzer portion of the tube was provided. Because of this the early ion–molecule studies were made with the instruments operating close to their upper pressure limits giving broad ion peaks because of scattering and retrograde sensitivity; that is, intensity decreased as the pressure was increased. Thus in the design of the new mass spectrometer, which by now we were proudly calling the Humble Chemical Physics Mass Spectrometer, we incorporated the highest pumping capacity of which we could conceive—250-L/s pumps on both the ion source envelope and the analyzer tube with only the final slit of the source ion optical system serving as the opening between the source region and the analyzer region. The pumps were connected to the mass spectrometer tube by 4-in.-diameter tubes, and the diameters of the source and analyzer envelopes were correspondingly large. Because of this the machine was looked upon by all who heard about it or eventually saw it as something of an extravagant monstrosity. Of course, the designer did not join in this opinion because of paternal pride. A picture of the machine in its very early days (about 1960) is shown in Figure 1. The picture gives a good view of the high capacity pumping system. It is clear from the size of the instrument that compactness was not a design goal. The operator in the picture is Wilburn Gieger, whose help with the construction and operation of the machine in Baytown contributed greatly to its success.

The machine came on stream (to use the parlance of the refinery in which it was located) in March 1959, and after some initial shakedown and familiarization runs a study of the ion–molecule reactions in ethylene was started. About three years previously we had done a study of ethylene using a small machine [2], finding some interesting results, and we were eager to restudy the system with the new machine, which we did. The study was very successful and yielded many interesting new results. Pressures up to 350 microns (0.35 torr) were used, and I was enough carried away by this accomplishment that I used the adjective "ultra-high" in referring to these pressures in the title of the paper I wrote describing the work [3]. Among other things we observed the occurrence of multiple-order reactions (as high as sixth order) to produce the $C_7H_{13}^+$ ion from ethylene. We were able to deduce that the rate constants for ternary reactions were of the order of 10^{-27} $cm^3/(mol \cdot s)$ and the rate constants for the decompositions of intermediate complexes were on the order of 10^7 s^{-1}. It was clear that opening up this high-pressure regime significantly extended the range and types of ion–molecule reactions which could be studied.

In spite of this promise, it was several years before the really high pressure capabilities of the machine were used in our studies. And the reason is that we were seduced by a fascinating diversion. It is true that a study of ion–molecule reactions in methane up to an ionization chamber pressure of 0.35 torr was made [4], and a similar study was made with ethane, propane, and butane [5], but for a period of several years our main research effort was in the direction of the diversion. Shortly after the ethylene study we had discovered (stumbled on is perhaps not an inappropriate characterization) some very unexpected ionic reactions

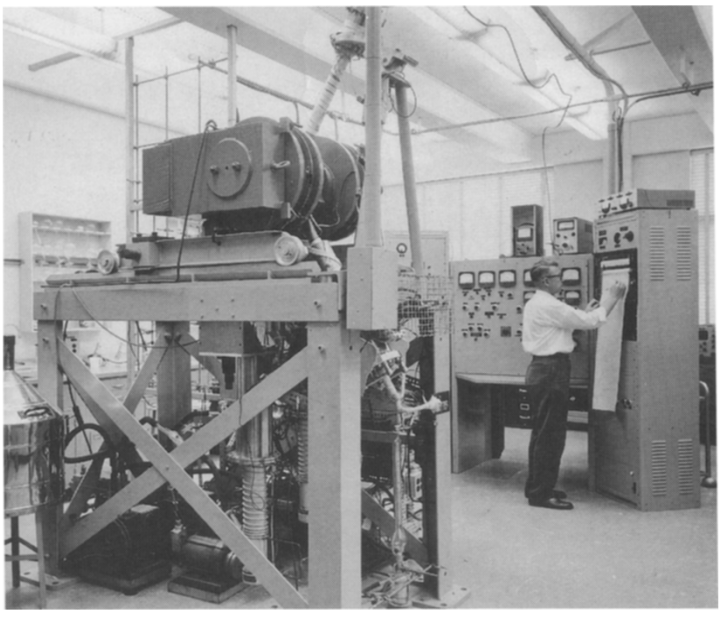

Figure 1. Humble Chemical Physics Mass Spectrometer, Humble Oil and Refining Co., Baytown, Texas, ca. 1960. The operator is Wilburn Gieger. Reprinted with permission from *Journal of the American Chemical Society*, **1965**, *87*, 3291. © 1965 American Chemical Society.

involving rare gas ions. For example, we discovered the existence of $Xe(CH_4)^{+\cdot}$ [6]. This even antedated the first discovery by Neil Bartlett in 1962 of the production of stable compounds involving rare gas atoms, so our discovery was of much interest. As an aside, I presented a paper on the $Xe(CH_4)^{+\cdot}$ work at the Second International Conference on Mass Spectrometry in Oxford in 1961, and the chairman of the session was so captivated by the material that he forgot the time, and I inadvertently spoke for five minutes more than I had been allotted.

We published several interesting papers on this general subject, but by the end of 1964 a gnawing worry began to assail me, and this worry had to do with relevance. Relevance is a term (other words to express the same concept doubtless exist) which is of importance in almost any scientific laboratory which is part of or is supported by a goal-oriented organization. Because of some corporate realignments the laboratory in which I worked was now supported by Esso (now Exxon), and Esso's goal was to find petroleum, process it, and sell the products. By several different means it was made known that the research work to be done in the corporation should be relevant to that goal. Up to that time we working in chemical physics mass spectrometry had had just about absolute freedom to do what we wanted, and we were given generous support. The work we were doing with rare gas ions was good research, but it had a very academic flavor, and I thought the probability low that it would have much impact on the refining of petroleum. No real pressure was brought to bear on us by the company concerning the relevance matter, but I thought that the relevancy request by the company was reasonable, and I supported it. It seemed to me that the best way of being relevant while doing basic scientific work was to revert back to using our fine machine to study ionic reactions in hydrocarbons. We thought that studying such reactions at increasingly high pressures might give us information about ionic reactions in hydrocarbons in condensed phase, which would certainly be both relevant and of real scientific interest. A secondary consideration caused us to work further with methane. A concern among some hydrocarbon chemists at the time was that there ought to be something better to do with the vast amounts of methane then available (the supply looked inexhaustible in the early 1960s) than just burn it as natural gas. We wondered if perhaps these marvelous new ion–molecule reactions might serve to convert lowly methane into something more useful and profitable. So we decided to switch our main research effort to a really high pressure study of the ion–molecule reactions in methane.

It is probably desirable at this time to define who were the "we" that I refer to repeatedly in this paper. The initial workers in the group were Joe Franklin and myself. Fred Lampe joined us in about 1954, and he left in 1960 to take a position at Penn State. Jean Futrell was in effect part of the group, although his main assignment was radiation chemistry. He was in residence in the period 1958–1959, after which he left to meet a military service obligation. All of these dates are from memory, and some may be in error by a year or so. Burnaby Munson joined the group in about 1960 to take Fred Lampe's place. Joe Franklin left in 1964 to become the first Robert A. Welch Professor at Rice University. So in the period which I am now discussing, which is the period immediately prior to the discovery of chemical ionization, the two remaining workers in the group were Burnaby and myself.

As I mentioned above, in previous studies we had achieved operation of the mass spectrometer at pres-

sures up to about 0.35 torr, and we now modified the instrument to attempt to operate at pressures higher than this. This involved decreasing the size of the electron entrance and ion exit slits in the ionization chamber of the machine and making sure that the chamber was as gas tight as possible otherwise. The new dimensions of the two slits were 0.05×3 mm and 0.05×5 mm, respectively. The electron current entering the ionization chamber was only 0.05 μA, which was partly the consequence of the small electron entrance slit, but also partly because the electron emission current was only about 6 μA. This low current was primarily the consequence of the practice in those days of using low emission currents to prolong the life of the filament. This was not really unwarranted, since in many machines a half day or more was required to change a filament. Our situation was exacerbated by the fact that we were using iridium for the filament for fear that the high pressure we were striving for would cause rapid deterioration of a tungsten or rhenium filament. The electron emissivity of iridium is quite low.

The first important discovery that we made, although we really didn't appreciate it, was that the ions found in methane at high pressure depended strongly on the presence of even quite small amounts of impurities. Water is a universal impurity in mass spectrometry, and ethane is found in small amounts in even the best grade commercial methane. Our goal was to get the high-pressure spectrum of pure methane, so the best available grade of commercial methane was subjected to a rigorous purification procedure. Methane was condensed in liquid nitrogen, and a center cut of this was then distilled onto Linde 5A molecular sieve maintained at liquid nitrogen temperature. The material sorbed on the sieve was distilled off and again a center cut was collected and stored in a glass vessel. The apparatus, including the sieve, was evacuated for 12 h prior to use, and immediately before the purification it was heated to 350 °C while being evacuated. The temperature of the glass storage vessel was also raised during evacuation to reduce sorption of impurities on the walls. Material sorbed on the interior surfaces of the mass spectrometer and the gas inlet lines also caused difficulties, and really satisfactory measurements were obtained only after the mass spectrometer had been in continuous use in CH_4 service for several weeks.

With these precautions some beautiful spectra of methane were obtained at pressures up to 2 torr. Figure 2 shows the relative concentrations of the important ions from methane as a function of ionization chamber pressure, and Figure 3 shows the relative concentration of $C_2H_5^+$ as a function of ionization chamber pressure including individual experimental points taken over a period of 2 months. The high degree of reproducibility was very gratifying. Both Figures 2 and 3 are taken from ref. 7. The lack of variation of the relative intensities of CH_5^+ and $C_2H_5^+$ above about 0.1 torr shows that these ions do not react with methane and thus will have a long lifetime in methane. We

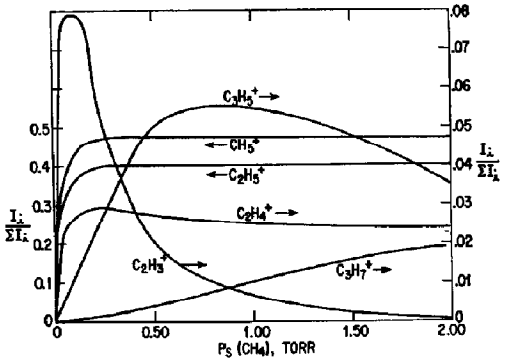

Figure 2. Relative intensities of ions from CH_4 as a function of CH_4 pressure. Reprinted with permission from *Journal of the American Chemical Society*, 1965, *87*, 3291. © 1965 American Chemical Society.

thought that this was the most important conclusion to be drawn from the experiment, but in the paper we wrote describing the research [7] we stated just in passing that we estimated the water content of the methane to be about 0.01%, but at a pressure of 2 torr the H_3O^+ ion comprised about 1.5% of the total ionization of the system, and to quote directly, "thus providing an illustration of the high probability of proton attachment to water and the relatively large number of collisions the ions make in the ionization chamber at high pressure." In retrospect this clearly was a manifestation of CI, although of course we did not recognize it as such at the time.

However, it was clear that interesting reactions with small amounts of impurities were occurring and that an investigation directed specifically at the effects of various impurities on the high-pressure methane spectrum was in order. Since we were in a petroleum company we were strongly interested in hydrocarbons, so the additives to methane that we first investigated were ethane and propane [8]. The technique used in those days was to make up a mixture of methane with a small amount of the additive (we used 1%) and measure the spectra of the mixture as a function of the pressure of the mixture in the ionization chamber of the mass spectrometer. Under these conditions the rel-

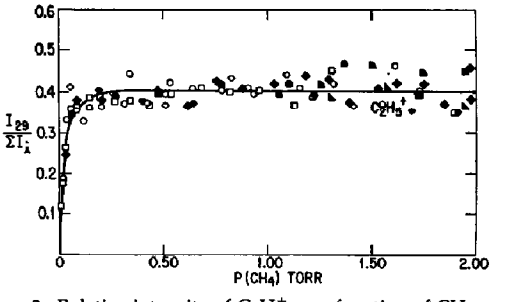

Figure 3. Relative intensity of $C_2H_5^+$ as a function of CH_4 source pressure showing experimental points. These were taken over a period of several months. Reprinted with permission from *Journal of the American Chemical Society*, 1965, *87*, 3297. © 1965 American Chemical Society.

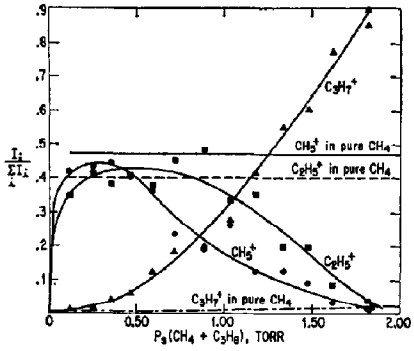

Figure 4. Intensities of ions from the mixture CH_4 + 1% C_3H_8 as a function of pressure. From ref. 8.

ative intensities of ions formed by ion–molecule reactions increased with increasing pressure, and the relative intensities of ions consumed by ion–molecule reactions decreased. Figure 4 shows a plot of the relative concentrations of CH_5^+, $C_2H_5^+$, and $C_3H_7^+$ as a function of the pressure of a mixture of methane with 1% propane. Clearly, both CH_5^+ and $C_2H_5^+$ react with propane to produce $C_3H_7^+$, which comes to dominate the spectrum at high pressures. In fact it is for all practical purposes the only ion produced from propane by these ion–molecule reactions, and the very large difference between this spectrum and that produced in propane by EI certainly did not escape our attention and interest. The intensity of the molecule-ion in the EI spectrum of propane is not particularly small, but it does not comprise the major fraction of the total ionization, and this difference between the EI spectrum and that which we produced by ion–molecule reactions with ions from methane was really most interesting.

We then moved on to *n*-butane as an additive and found the same general results as with propane; that is, as the pressure of the mixture of butane and methane was increased the intensity of the butyl ion ($C_4H_9^+$, m/z 57) steadily increased and became virtually the sole ion in the spectrum.

This work was not published as such, but we really were beginning to get excited. It had been known from the National Bureau of Standards compilation of spectra (1947) that the relative intensity of the molecule-ion in the EI spectra of normal paraffin hydrocarbons undergoes a monotonic decrease as the number of carbon atoms in the molecule increases, disappearing at about C_{36}. By the time one gets to C_6 (*n*-hexane), the molecule-ion intensity is quite small—only a few percent of the base peak and, of course, less of the total ionization. Thus we decided to make what we considered to be a crucial experiment, namely, measuring the spectra of a mixture of *n*-hexane in methane as a function of pressure. I can still remember the interest (and trepidation) with which we monitored the $C_6H_{13}^+$ ion intensity as the pressure of the mixture in the mass spectrometer was increased. At the conclusion of the experiment we observed with great excitement that, once again, the alkyl ion produced by removing a hydride ion from the parent molecule dominated, and a really new and potentially important phenomenon was at hand. Indeed, we then even tried a highly branched paraffin which gave no molecular ion by EI (2,2-dimethylbutane), and we found to our delight that the methane ionization spectrum contained an appreciable amount of quasi-molecular ion ($[M-1]^+$).

The excitement we felt had two aspects. The theoretical one was that the extensive molecule-ion decomposition observed under EI with the straight-chain paraffin hydrocarbons (which were just about the only relatively large, linear molecules then amenable to mass spectrometric investigation) was not occurring with the type of ionization occurring in our systems. We immediately recognized that the ions produced by the abstraction of a hydride ion from the paraffin hydrocarbon were even-electron ions rather than the odd-electron ions produced initially by EI, and the stabilities and decomposition paths of the two might well be different, with more stability to be found in the former. We also thought it quite likely that the amount of energy transferred to the quasi-molecular ions in the ion–molecule reactions was smaller than in the corresponding EI case. That is to say, the ionization was softer, although I don't think that this term had as yet been invented, and it certainly had not been applied to mass spectrometry. We recognized the importance and were very excited by the apparent existence of a new type of gaseous ionization and one with properties different from those of EI. At the time photoionization had been used in some basic mass spectrometric studies, and field ionization was about to be discovered, but for practical purposes EI was the overwhelmingly dominant type of ionization available to organic mass spectrometrists. While it had obvious strengths, it also had some weaknesses that had to be accepted because of the lack of a practical alternative.

The second aspect of our excitement was a practical one. Mass spectrometers in a petroleum company laboratory were analytical instruments, and while the basic research that we were doing was an exception to this generalization, we were always aware of the analytical activities and problems in which our distinguished analytical colleagues at Baytown (Earl Lumpkin and Tom Aczel) were involved, and we were eager for our basic studies to contribute to the greatest extent possible to the solution of these problems. About ten years earlier we had made a basic research contribution to analytical problems in the form of low voltage ionization mass spectrometry. This technique has since been developed by Earl Lumpkin and especially by Tom Aczel, and is still in extensive use, but that is another story. In any event, the spectra formed in *n*-paraffins by reactions with the ions from methane seemed to offer a way of solving an important problem in hydrocarbon chemistry, namely, finding a quick method for obtaining the carbon number distribution in a mixture of saturated hydrocarbons. We had succeeded in doing this for unsaturated and aromatic

compounds with our low voltage EI method, but as I mentioned above, under EI the molecule-ion intensities in *n*-paraffins rapidly decrease as the size of the molecules increases. Furthermore, for branched paraffins the situation is worse: the decrease in molecule-ion intensities is more rapid, and for very highly branched paraffins it is zero even for small compounds, for example, neopentane. Because of their cyclic structure, naphthenes exhibit more intense molecule-ions but even with these compounds the intensities get weak as the molecules get quite large. In addition, there are quite a number of other types of compounds—amines, for example—which produce small or zero molecule-ions; in fact I have seen an estimate (in McLafferty's monograph?) that about 20% of organic compounds do not produce molecule-ions by EI. We wondered if perhaps our new method of ionization would provide a higher percentage of stable molecule-ions (actually quasi-molecular ions). However, I should point out that not many mass spectrometrists were interested in or even aware that a problem concerning molecule-ion stability existed. Perhaps the main thrust of basic organic mass spectrometry at the time was attempting to understand the decomposition reactions occurring under EI, and so what if some compounds had completely unstable molecule-ions? Deducing the structure of compounds from their mass spectra was a popular activity (to call it a game would be a bit pejorative), and fragmentation was generally looked upon as highly desirable. Our position as petroleum chemists gave us a different point of view. I might say that twenty-five more years in the real analytical world using various kinds of ionization techniques including CI leaves me still convinced of the importance of finding a molecule-ion or ions in the spectra of real analytical samples, particularly for new compounds or those for which no authentic spectrum is available.

In order further to investigate our interesting new ionization method a quicker and more convenient way of introducing the sample was needed. It was obvious that instead of making a mixture of sample and methane outside the mass spectrometer and introducing the mixture into the spectrometer, it would be easier to have separate introductions of each component (with the methane flowing continuously) so that the mixture would be made inside the spectrometer. Fortunately, in the original design of the mass spectrometer two separate sample introduction systems had been provided to deal with a possible need such as that which we now had. Thus the separate introduction of the methane and the sample could be accomplished quite easily, and we set out to make a survey of the spectra produced by different types of compounds. We also recognized at this early time that compounds other than methane could be used as the reactant; in particular we knew that *i*-butane and propane would be less energetic in producing product ions and that hydrogen would be more energetic. We further recognized that one could mimic EI spectra by using substances such as nitrogen and nitric oxide which would produce odd-electron ions as reactants. We guessed that analogous negative ion reactions would occur. A small number of experiments to establish the validity of these expectations were made.

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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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COMMENTS OF REFEREE I

AUTHOR: Munson and Field 133

TITLE: Chemical Ionization Mass Spectrometry I ...

COMMENTS:

This is a very carelessly written paper and a serious waste of a reviewer's time. In general, the arrangement must be improved and considerably more precise language employed before I would consider it worth publishing. Have the authors really read the submitted manuscript?

Page 7, 2nd paragraph - This paragraph is utterly ridiculous in both content and construction. The entire paragraph should be omitted. If the authors insist on including the first sentence, please make it "gallium-covered procelain frit."

p.9, L. 20. The authors must be joking! What does the statement, " - electron impact ionization is often times satisfactory" mean? Also the reference to the use of H_2 needs further explanation.

pp 13, et seq. I can not argue with the author's conjectures regarding the origin of the spectra. However, despite occasional references to heats of formation and exothermic reactions, conjecture is all it is. When some observations (e.g. p. 31) are "explained by the use of impure materials I think one should give serious consideration to the value of the work and the usefulness of publication.

Figure 5. Reviewer's comments on the manuscript first introducing chemical ionization. In spite of the review, the manuscript was published [9].

The results of our survey of different compounds using methane was excitingly successful, for we found strong quasi-molecule-ions and even some useful, understandable fragmentations. We prepared a manuscript describing our work and submitted it to *JACS* as an article. We were so convinced of the importance of the work that in addition we sent copies of the manuscript to about 50 mass spectrometrist friends, which is something I had never done before nor have done since. In writing the paper it became clear that a short, descriptive, snappy name for our new ionization technique was needed, and since the product ions of interest were formed by chemical reactions, we hit on the name "chemical ionization," which in retrospect was a felicitous choice. We worried that a confusion with the term "chemi-ionization" (as in the production of CHO^+ from excited O and CH) might occur, but the only objection or problem of which I ever heard was from Viktor Talrose, and I assume that this had more to do with the translation into Russian than with the English term.

The *JACS* reviewer who dealt with the paper was very negatively impressed with our efforts, and I give as Figure 5 a reproduction of his extraordinar-

ily derogatory review. The manuscript was in fact well written, and I can only conclude that the newness of the material exceeded the scope of the reviewer's imagination and comprehension. This matter now seems to be only amusing, but at the time our feelings were a good deal stronger. We made a few cosmetic changes in the manuscript, shortening it a bit in noncritical places (always a desirable tactic with negative reviews), and we resubmitted it with a stiffish letter to the Editor giving our views of the validity of the reviewer's comments. We prevailed, and the paper was published [9].

I need not do more here than to state that following this rather contentious introduction the CI method has grown to have widespread use. About two years ago I did a search using the CA Online facility and found that as of that time approximately 1500 articles had been written wherein the term "chemical ionization" was used in the title or the abstract. The only sad aspect of the whole matter is that Humble (Esso, Exxon) as far as I know has not profited from this work as much as one would have liked. At Humble we were successful in getting a strong patent on the CI method, but Esso saw fit to sell the rights for the patent for a really trivial amount of money, and the purchaser realized the not inconsiderable royalties (by scientific instrument manufacturing standards) that the patent generated. Furthermore, our hopes that the method would be particularly useful in the petroleum industry for the determination of carbon number distributions in saturates seems not to have been realized. However, from our point of view as discoverers of the technique, its success in larger contexts than hydrocarbon chemistry, that is, in organic chemistry in general and in biochemistry, has been tremendously gratifying to me and, I am sure, to Burnaby.

References

1. Talrose, V. L.; Lyubimova, A. K. *Dokl. Akad. Nauk SSSR* **1952**, *86*, 909.
2. Field, F. H.; Franklin, J. L.; Lampe, F. W. *J. Am. Chem. Soc.* **1957**, *79*, 2419.
3. Field, F. H. *J. Am. Chem. Soc.*, **1961**, *83*, 1523.
4. Field, F. H.; Franklin, J. L.; Munson, M. S. B. *J. Am. Chem. Soc.* **1963**, *85*, 3575.
5. Munson, M. S. B.; Franklin, J. L.; Field, F. H. *J. Phys. Chem.* **1964**, *68*, 3098.
6. Field, F. H.; Franklin, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 4509.
7. Field, F. H.; Munson, M. S. B. *J. Am. Chem. Soc.* **1965**, *87*, 3289.
8. Munson, M. S. B.; Field, F. H. *J. Am. Chem. Soc.* **1965**, *87*, 3294.
9. Munson, M. S. B.; Field, F. H. *J. Am. Chem. Soc.* **1966**, *88*, 2621.